Supporting Information for

Understanding the Reaction Mechanism of *anti*-Addition of (NHC)Au(I)-H and (NHC)Au(I)-F across Alkyne

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Figures and Tables

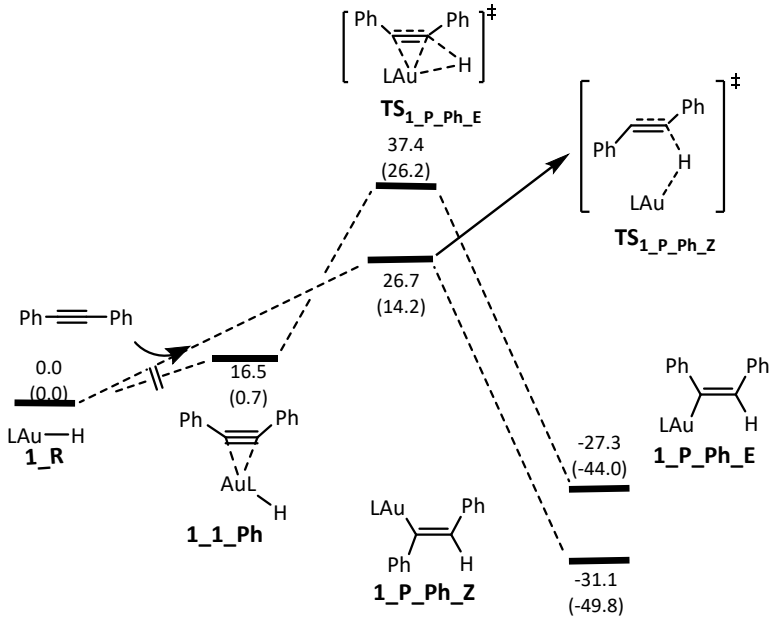

Fig. S1 Gibbs energy profile for addition reaction of LAu-H across PhC≡CPh. Relative Gibbs energies and relative electronic energies (in parenthesis) are given in kcal/mol. See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L.

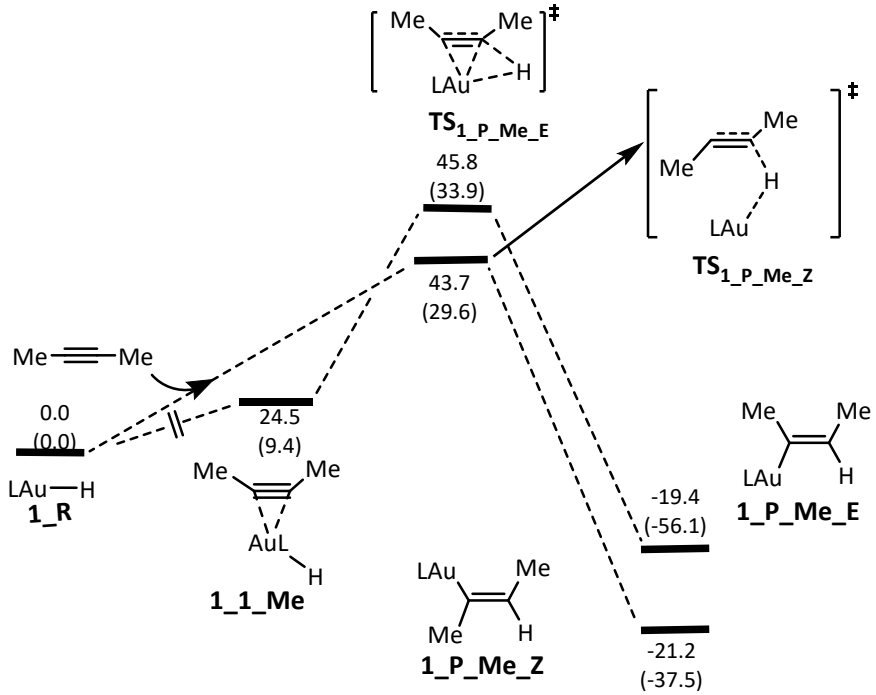

Fig. S2 Gibbs energy profile for addition reaction of LAu-H across MeC≡CMe. Relative Gibbs energies and relative electronic energies (in parenthesis) are given in kcal/mol. See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L.

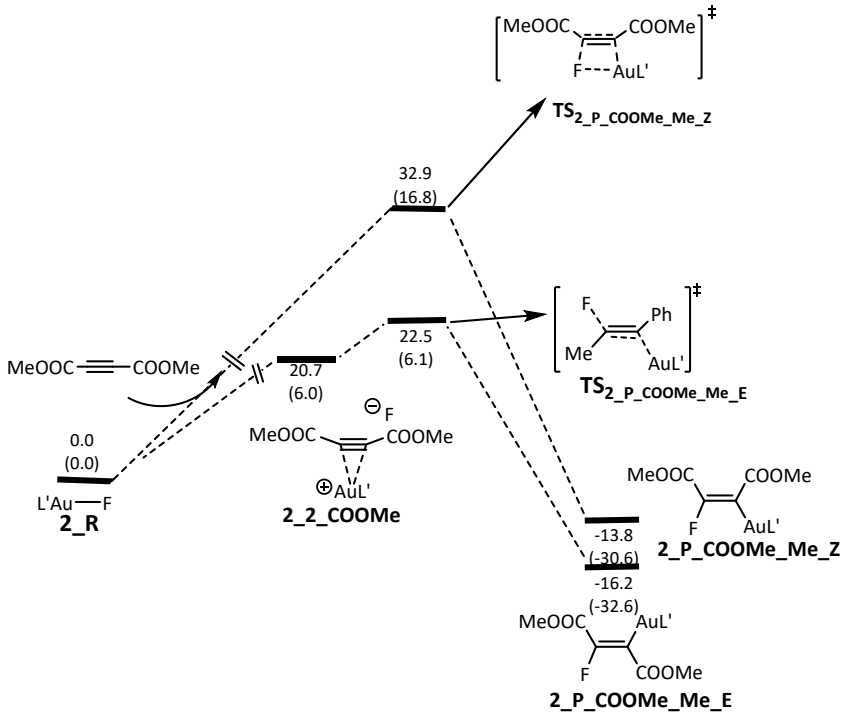

Fig. S3 Gibbs energy profile for addition reaction of L′Au-F across MeOOCC≡CCOOMe. Relative Gibbs energies and relative electronic energies (in parenthesis) are given in kcal/mol. See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L′.

Table 1 $\Delta G_{\mathbf{TS1\_P\_Ar\_Z}}$ of addition reactions of LAu-H across ArC≡CAr (see Figure S1 or S2 for the structure label **TS1_P_Ar_Z**). See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L.

Ar	$\Delta G_{\mathbf{TS1\_P\_Ar\_Z}}$ (kcal/mol)
C_6H_4-*p*-NO_2	18.2
C_6H_4-*p*-CN	19.7
C_6H_4-*p*-NMe_2	33.5
C_6H_4-*p*-OMe	32.9

Table 2 $\Delta G_{\mathbf{2\_2\_Ar}}$ and $\Delta G_{\mathbf{TS2\_P\_Ar\_E}}$ of addition reactions of L′Au-F across ArC≡CAr (see Figure S3 for the structure labels **2_2_Ar** and **TS2_P_Ar_E**). See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L′.

Ar	$\Delta G_{\mathbf{2\_2\_Ar}}$ (kcal/mol)	$\Delta G_{\mathbf{TS2\_P\_Ar\_E}}$ (kcal/mol)
C_6H_4-*p*-NO_2	13.8	19.3
C_6H_4-*p*-CN	14.1	19.3
C_6H_4-*p*-NMe_2	9.2	17.4
C_6H_4-*p*-OMe	12.0	19.6

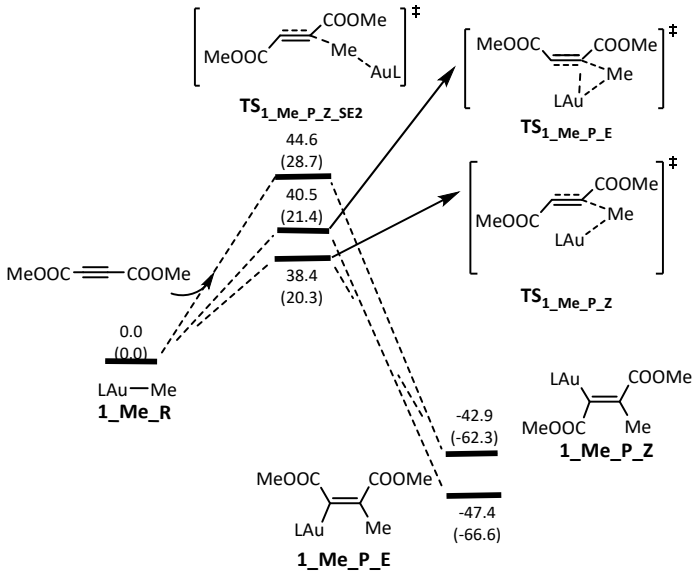

Fig. S4 Gibbs energy profile for addition reaction of LAu-Me across MeOOCC≡CCOOMe. Relative Gibbs energies and relative electronic energies (in parenthesis) are given in kcal/mol. See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L.

Table S3 Gibbs energies of selected intermediates and transition states calculated for addition reactions of L′Au-X (X = Cl, Br and I) across PhC≡CMe. See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L′.

	Syn		**Anti**	
L′Au-X/ΔG (kcal/mol)	**Reaction barriers ($\Delta G_{TS2\_P\_Me\_Z}$)**	**Reaction energies ($\Delta G_{2\_P\_Me\_Z}$)**	**Reaction barriers ($\Delta G_{TS2\_P\_Me\_Z}$)**	**Reaction energies ($\Delta G_{2\_P\_Me\_Z}$)**
Cl	38.3	16.7	26.0	15.3
Br	40.5	18.5	27.8	16.2
I	37.1	20.7	25.8	19.5

Table S4 Calculated barriers and reaction energies for the addition reactions of LAu-H, (CAAC)Au-H and PPh_3Au-H with MeOOCC≡CCOOMe.

	Syn-addition		**Anti-addition**	
(Ligand)Au-H / ΔG (kcal/mol)	Reaction barrier ΔG‡ **($TS_{1\_P\_E}$)**	Reaction energy **(1_P_E)**	Reaction barrier ΔG‡ **($TS_{1\_P\_Z}$)**	Reaction energy **(1_P_Z)**
Ligand = L	27.5	-36.8	21.6	-40.7
Ligand = CAAC	32.1	-38.8	25.6	-40.5
Ligand = PPh_3	31.1	-39.1	21.1	-41.5

L: See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L.
CAAC: ^{Ad}CAAC from Ref [16] in the main text.

Table S5 Calculated barriers and reaction energies for the addition reactions of LAu-H, (CAAC)Au-H and PPh_3Au-H with MeC≡CPh.

	Syn-addition		**Anti-addition**	
(Ligand)Au-F / ΔG (kcal/mol)	Reaction barrier ΔG‡ **(TS2_P_Me_Z)**	Reaction energy **(2_P_Me_Z)**	Reaction barrier ΔG‡ **(TS2_P_Me_E)**	Reaction energy **(2_P_Me_E)**
Ligand = L′	33.7	-0.9	20.8	-1.5
Ligand = CAAC	32.1	-1.1	22.0	-2.7
Ligand = PPh_3	32.1	-1.3	26.5	-1.4

L′: See Scheme 1 in the main text for the structure of the N-heterocyclic carbene (NHC) ligand L′.
CAAC: ^{Ad}CAAC from Ref [16] in the main text.